Enclosure 13

(12) UK Patent Application (19) GB (11) 2 173 496 A

(43) Application published 15 Oct 1986

(21) Application No 8508829

(22) Date of filing 4 Apr 1985

(51) INT CL[4]
C07D 303/08

(52) Domestic classification (Edition H):
C2C 1300 215 246 247 253 25Y 305 313 31Y 339 411 413 414 430 VT ZA

(56) Documents cited
None

(58) Field of search
C2C

(71) Applicants
Instytut Ciezkiej Syntezy Orgaricznej BLACHOWNIA (Poland),
Kedzierzyn-Kozle, Poland.
Zaklady Chemiczne ORGANIKA-ZACHEM (Poland),
Bydgoszcz, Aleja Ludowego Wojska Polskiego 65, Poland

(72) Inventors
Andrzej Brzezicki
Janusz Dula
Zofia Pokorska
Marian Spadlo
Manfred Stajszczyk
Jerzy Wasilewski
Eugeniusz Wojcik
Marek Usakiewicz
Tadeusz Wilusz
Grzegorz Lewandowski
Stanislaw Gawrych

(74) Agent and/or Address for Service
J A Kemp & Co,
14 South Square, Gray's Inn, London WC2R 5EU

(54) Method for producing epichlorohydrin

(57) Epichlorohydrin is produced by the epoxidation of a mixture composed of 70% 1,2-dichloropropanols and 30% 1,3-dichloropropanols in an aqueous solution in a concentration of 1,8–4 wt% with milk of lime at a temperature of 38–45°C at a pH up to 10–12. The process is effected in a plate column, and the epoxidation reaction is conducted simultaneously with rectifying distillation of the epichlorohydrin formed using live steam. The process is conducted in the plate column provided with at least 19 plates and the dichloropropanol solution is introduced onto the second or third plate counting from the top. The time of reaction in the liquid phase is 25–35 s, and epichlorohydrin contained in the steam mixture is received from the column top at a pressure of 47–57 kPa and a temperature of 80–85°C. Live steam is fed into the column bottom so as to maintain the evaporation degree within a range of 0.045–0.080.

GB 2 173 496 A

SPECIFICATION

Method for producing epichlorohydrin

This invention relates to a method for producing epichlorohydrin from a mixture of dichloropropanols.

In industrial practice, epichlorohydrin is obtained by the chlorohydrination of allyl chloride to dichloropropanols in a diluted aqueous medium using hypochlorous acid, and the thus produced dichloropropanols are dehydrochlorinated to epichlorohydrin with milk of lime or less often sodium hydroxide.

In the first stage of synthesis, on account of side reactions between allyl chloride and chlorine and a poor solubility of the former in water, the ratios of introduced chlorine, allyl chloride and water should be such that chlorine is reacted completely and the concentration of dichloropropanols is not higher than 4 wt. % in the post-reaction solution. Only U.S. Patent Specification No. 2227948 is a concentration of dichloropropanols up to 10 wt.% claimed.

In the second stage of synthesis, it is essential that the reaction of epichlorohydrin to glycidol and further to glycerol is limited in order to obtain high selectivity.

There are many engineering solutions to the dehydrochlorination process of dichloropropanols to epichlorohydrin. U.S. Patent Specification No. 2177419 and West German Patent Specification No. 1593009 describe a reaction that is initially conducted in a tank-type reactor, into which milk of lime (an aqueous suspension of calcium hydroxide) is introduced, or in a cascade of tank-type reactors (Rumanian Patent Specification No. 56369), and the completion of reaction and the separation of crude epichlorohydrin occur in a stripping column heated directly by steam or by a surface evaporator. The stripping column operates under reduced pressure of 0.03 MPa.

Another method is known from U.S. Patent Specification No. 227948 and Great Britain Patent Specification No. 974164 in which the reaction is accomplished only in a stripping column, atmospheric or elevated pressure being used. The column vapour temperature is then 96–100°C and the weight ratio of distilled off epichlorohydrin to water is 9. The distillate from the column top forms two phases: an upper phase, water, which is recycled as reflux; and a bottom phase, crude epichlorohydrin, which is directed for purification. The enthalpy of vapours from the column top can additionally be utilized for preheating milk of lime fed to the dehydrochlorination process (according to U.S. Patent Specification No. 3527774). In the above-mentioned methods, the conversion yield of dichloropropanols to epichlorohydrin is within the range from 90–92.1%, the higher values being obtained in solutions in which only a stripping column is used.

In the method referred to in Great Britain Patent Specification No. 960023, an inert component, trichloropropane, is introduced into the dehydrochlorination process to improve conversion selectivity. However, the lack of data on dichloropropanol change does not permit the conversion yield of dichloropropanols to epichlorohydrin to be evaluated. The shortcoming of this method is the necessity of recycling the trichloropropane, which requires two additional rectifying systems to be used to separate the trichloropropane from the organic and inorganic phases.

In all the discussed solutions to the method of producing epichlorohydrin only the yield of conversion of dichloropropanols to epichlorohydrin or the process selectivity is determined, which does not fully characterize a given solution. For the quantity that determines the quality of the solution is the efficiency of the whole process, i.e. the epichlorohydrin output as a crude product received from the top of a stripping column. This quantity is always lower than the conversion yield of dichloropropanols to epichlorohydrin because losses of epichlorohydrin in the stripping column, in the form of the decoction directed to waste, are taken into account. The higher the epichlorohydrin output the lower the content of organic compounds in the wastes, so that the noxiousness of the latter to the natural environment is lower, which is of importance since the quantity of waste in the solutions discussed is about 100 times larger than that of the epichlorohydrin obtained.

The object of the present invention is to increase the output of epichlorohydrin in a process for dehydrochlorinating dichloropropanols conducted in a stripping column.

According to this invention, epichlorohydrin is produced by reacting a mixture composed of about 70% 1,2-dichloropropanols and about 30% 1,3-dichloropropanols in an aqueous solution having a concentration of 1.8–4 wt.% with milk of lime mixed at a temperature of 38°–45°C and at a pH up to 10–12, this value being maintained during the reaction, in a plate column provided with at least 19 plates, the reaction being conducted simultaneously with a rectifying distillation of the epichlorohydrin formed using live steam, and the dichloropropanol solution being introduced onto the second or third plate from the column top, the time of reaction on the column plate in the liquid phase being 25–35 s, the epichlorohydrin formed in the steam mixture being received from the column top at a pressure of 47–57 kPa and at a temperature of 80°–85°C, and the live steam being fed to the column bottom in an amount such as to ensure that the evaporation degree is maintained within a range of 0.045–0.080.

In the new process it is advantageous to receive epichlorohydrin from the column top at a

pressure of 50–54 kPa and a temperature of 80–83°C by feeding into the column bottom an amount of live steam such as to maintain the evaporation degree within the range of 0.055–0.070. The evaporation degree is defined as the ratio of total amount of moles of components that are removed from the plate supplied by the feed during steam phase to the quantity of moles of components fed onto this plate during liquid phase.

Lime milk is added to the reaction mixture in such an amount as to maintain its pH-value within the range of 10–12.

The time of the reaction in liquid phase on the column plate ranges from 25 to 35 s. This time is optimum on account of the rapid reaction of the 1,3-dichloropropanol isomer and the slower reaction of the 1,2-dichloropropanol isomer and, together with the rectifying distillation of epichlorohydrin which is formed more quickly from the isomer of 1,3-dichloropropanol, it hinders its further reacting to glycidol.

The delivery of the aqueous dichloropropanol solution onto the second or third column plate rather than onto the column top improves epichlorohydrin yield because of partial condensation of evaporated dichloropropanols by reflux. Increasing the number of plates above 19 is economically unprofitable since it does not markedly increase the yield of eipchlorohydrin but increases the cost of column.

Compared with known similar methods, the yield of epichlorohydrin in the new process is the highest amounting to 94%, and the conversion of dichloropropanols is above 98%. Moreover, the new method enables the amount of organic compounds to be minimized in aqueous solution removed from the column bottom as wastes. This amounts to about 0.047 wt. %.

In the two Examples which follow, a known industrial method of dichloropropanol epoxidation is described in Example I and the method of the present invention in Example II.

EXAMPLE I

A solution of dichloropropanols in an aqueous solution in the concentration of 2.3 wt. % at a temperature of 40°C, together with milk of lime in an amount such that the reaction pH-value is maintained within the range of 10 to 12, is fed into a pre-reactor. Also, live steam in an amount to ensure the reaction temperature of 50°C is added into the pre-reactor. The residence time of reaction mixture in the pre-reactor is 10 min. The reaction mixture is transferred by a pump from the pre-reactor to a column in which crude epichlorohydrin is separated. Parameters of the column operation: pressure within the top – 40 kPa, evaporation degree – 0.035, residence time for liquid phase in column – about 4.5 min.

The vapours from the column top are condensed in a condenser and separated in a distributor into a water layer returned as reflux to the column and an organic layer removed as crude epichlorohydrin. The yield of epichlorohydrin is 86%. The content of organic compounds is 0.19 wt. % in wastes.

EXAMPLE II

A solution of dichloropropanols in an aqueous solution of the concentration of 2.3 wt % at the temperature of 40°C mixed with lime milk to obtain a pH-value up to 10–12, is fed onto the second or third plate of a 19-plate rectifying column. Live steam is supplied under the 19-th column plate. Stream distillate is condensed in a condenser and separated in a distributer into a water layer recycled as reflux to the column top and an organic layer removed as crude epichlorohydrin. Parameters of the column operation : pressure within the top 52 kPa, evaporation degree 0.07, temperature of the top 82°C, temperature of the bottom 91°C, residence time for liquid phase on column plate – 29.8 s. The yield of epichlorohydrin is 94% and the content of organic compounds in wastes is 0.047 wt.%.

CLAIMS

1. A method for producing epichlorohydrin which comprises reacting a mixture of about 70% 1,2-dichloropropanol and about 30% 1,3-dichloropropanol in an aqueous solution having a concentration of 1.8–4 wt.% with milk of lime of 38–45°C and at a pH up to 10–12, in a plate column provided with at least 19 plates, the reaction being conducted simultaneously with a rectifying distillation of the epichlorohydrin formed using live steam, the aqueous dichloropropanol solution being introduced onto the second or third plate from the column top, the time of reaction on the column plate in the liquid phase being 25–35 s, the epichlorohydrin formed being received at the column top at a pressure of 47–57 kPa, and at a temperature of 80–85°C; and the live steam being fed to the column bottom so as to maintain an evaporation degree within the range of 0.045–0.080.

2. A method according to claim 1 in which the epichlorohydrin reaches the column top at a pressure of 50–54 kPa and a temperature of 82–83°C.

3. A method according to claim 1 or 2 in which the rate of injection of live steam is such as to maintain an evaporation degree of 0.055 to 0.070.

4. A method according to claim 1 substantially as hereinbefore described in Example II.

5. Epichlorohydrin when produced by the method of any of claims 1 to 4.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.